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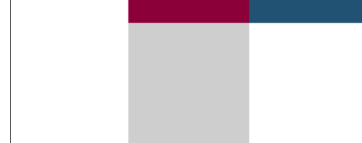
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Phase space investigation of the lithium amide halides.

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Abstract

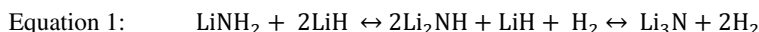
An investigation has been carried out into the lower limits of halide incorporation in lithium amide (LiNH₂). It was found that the lithium amide iodide Li₃(NH₂)₂I was unable to accommodate any variation in stoichiometry. In contrast, some variation in stoichiometry was accommodated in Li₇(NH₂)₆Br, as shown by a decrease in unit cell volume when the bromide content was reduced. The amide chloride Li₄(NH₂)₃Cl was found to adopt either a rhombohedral or a cubic structure depending on the reaction conditions. Reduction in chloride content generally resulted in a mixture of phases, but a new rhombohedral phase with the stoichiometry Li₇(NH₂)₆Cl was observed. In comparison to LiNH₂, this new low-chloride phase exhibited similar improved hydrogen desorption properties as Li₄(NH₂)₃Cl but with a much reduced weight penalty through addition of chloride. Attempts to dope lithium amide with fluoride ions have so far proved unsuccessful.

Keywords: hydrogen storage materials; hydrogen; powder X-ray diffraction; lithium amide halides

1. Introduction

A large range of materials have been shown to store hydrogen reversibly at a higher density than in its gaseous or liquid form. Mobile applications require the material to be light, causing an increasing focus on the complex hydrides of lighter elements such as aluminium (alanates) [1], boron (borohydrides) [2] and, by analogy, nitrogen (amides) [3, 4]. However, despite exhibiting favourable thermodynamics for reversible desorption and absorption of hydrogen, these materials suffer from slow kinetics. Although improvements have been seen on addition of transition metal catalysts [1], this problem is yet to be satisfactorily resolved.

The lithium amide system is one such light metal system that is considered promising for hydrogen storage. Thermal decomposition of LiNH₂ alone evolves ammonia rather than hydrogen, but addition of lithium hydride (LiH) creates a pathway that can experimentally produce up to 9.3 wt% of hydrogen in the two steps shown in Equation 1 [3]. The second of these requires temperatures above 320°C and is not generally considered to be a viable hydrogen storage reaction [4]. However, the first stage alone has been shown to reversibly release up to 6.3 wt% H₂ [3].



Anderson *et al.* [5] found that the addition of lithium or magnesium halides to lithium amide results in the formation of new amide halide phases that exhibit not only reduced temperatures of hydrogen release, with little or no release of ammonia, on reaction with LiH or MgH₂, but also increased ionic conductivity relative to LiNH₂. However, the addition of heavy halide anions reduces the gravimetric hydrogen capacity of the material.

This study investigates the phase space of lithium amide halides with the aim of reducing the gravimetric penalty as much as possible whilst maintaining the observed improvements in the hydrogen storage properties.

2. Materials and methods

Lithium amide (Sigma–Aldrich, 95%) was used without further purification. Anhydrous lithium halides (Sigma–Aldrich, $\geq 98\%$) were dried at 300°C under high vacuum (1×10^{-6} mbar) for 24 h prior to use. All manipulations were performed in an argon-atmosphere glove box. Amide halides were synthesized by grinding the appropriate halide with LiNH_2 in the desired molar ratio, placing the reaction mixture into a quartz tube, and heating under an argon flow (1 bar) at the required temperature for the specified reaction time.

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer in transmission geometry with a $\text{Cu-K}\alpha 1$ X-ray source. Samples were sealed from the atmosphere between two pieces of amorphous tape. Powder XRD data for structural investigations were collected on a Siemens D5000 diffractometer in capillary mode with a $\text{Cu-K}\alpha 1$ X-ray source. Samples were sealed into polyimide capillaries, allowing for long data collection times without degradation. Powder synchrotron X-ray diffraction data were collected on beamline I11 at the Diamond light source, Oxfordshire [6]. Samples were sealed in borosilicate glass capillaries to prevent degradation during transportation and measurement. Powder XRD data were analysed using the computer program Topas [7], and structure solution was performed using Rietveld refinement of candidate models devised with the help of simulated annealing methods.

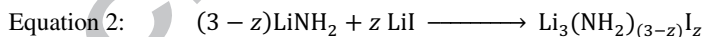
Temperature programmed desorption with mass spectrometry (TPD–MS) data were collected using a home-built TPD apparatus described previously [8], coupled to a quadrupole mass spectrometer (HPR-20, Hiden Analytical). Samples were heated at 2°C min^{-1} to 400°C and held at temperature for 1 hour before cooling.

3. Results and Discussion

3.1 Lithium amide iodide

Lithium amide reacts with lithium iodide at an $\text{NH}_2^- : \text{I}^-$ ratio of 2:1 to form the amide iodide $\text{Li}_3(\text{NH}_2)_2\text{I}$ [5,9]. Rietveld refinement against powder synchrotron XRD data confirmed the structure reported previously [9] of a hexagonal unit cell with $a = 7.0650(9) \text{ \AA}$, $c = 11.521(1) \text{ \AA}$.

The reaction, shown in Equation 2, between lithium amide and lithium iodide was carried out at 150°C over a range of stoichiometries ($0.5 \leq z \leq 1$) for a reaction time of twelve hours.



For all the values of z studied, LiNH_2 was observed in the XRD patterns alongside the amide iodide. Figure 1 shows the cell volume of the amide iodide products for values of z between 0.5 and 1. It can be seen that there is, within error, no systematic variation in the cell volume of the amide iodide formed in these reactions.

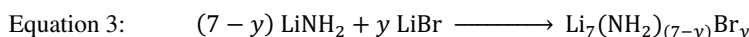
Analysis of the diffraction patterns of the products showed both $\text{Li}_3(\text{NH}_2)_2\text{I}$ and LiNH_2 present where the value of z was less than one. The consistency in the lattice parameter and the presence of the starting materials in the products indicate that variations in composition cannot readily be accommodated in this structure.

3.2 Lithium amide bromide

Lithium amide reacts with lithium bromide at an $\text{NH}_2^- : \text{Br}^-$ ratio of 1:1 to form LiNH_2Br [5,10], whose low temperature hydrogen desorption mechanism has recently been studied in some detail [11]. At a lower bromide

content, it also reacts at a ratio of 6:1 to form $\text{Li}_7(\text{NH}_2)_6\text{Br}$. Rietveld refinement against powder synchrotron XRD data has confirmed the preliminary structure reported previously for $\text{Li}_7(\text{NH}_2)_6\text{Br}$ [5] of a hexagonal unit cell with $a = 9.84893(3) \text{ \AA}$, $c = 8.9845(3) \text{ \AA}$ and rhombohedral symmetry.

The limits of the bromide content in the structure were investigated. The reaction between lithium amide and lithium bromide, shown in Equation 3, was carried out at 250°C over a range of compositions, between $y = 0.6$ and 2.33 , for a reaction time of twelve hours.

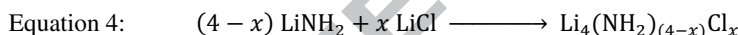


Increasing the bromide level above $y = 1$ reduced the yield of the amide bromide and large peaks for LiBr were observed in the X-ray diffraction pattern of the product, indicating that the structure cannot accommodate any additional Br^- ions. The product from the reaction at the $\text{NH}_2^-:\text{Br}^-$ ratio 2:1 ($y = 2.33$) contained mainly unreacted starting materials.

Reducing the bromide content below $y = 1$ decreased the yield of the amide bromide, with LiNH_2 observed in the XRD patterns of the products. A decrease in the cell volume of the amide bromide was observed as y was reduced (Figure 2), with an overall contraction of 1.24% . However, the presence of LiNH_2 in the X-ray diffraction patterns of the products means that it is not possible to calculate the exact extent of the non-stoichiometry directly from the reactant ratios.

3.3 Lithium amide chloride

Lithium amide reacts with lithium chloride at an $\text{NH}_2^-:\text{Cl}^-$ ratio of 3:1, forming $\text{Li}_4(\text{NH}_2)_3\text{Cl}$ [5]. After a reaction time of one hour a rhombohedral $R\bar{3}$ phase is formed and after twelve hours the compound takes a cubic $I2_13$ form [5]. The reaction shown in equation 4 was carried out over a range of compositions between $x = 0.5$ and 1.75 at 400°C for both one and twelve hours to investigate the effect of composition on the structure of amide chlorides under both kinetic and thermodynamic conditions.



For both reaction times, increasing x above one caused LiCl to be observed in the reaction products, suggesting that no additional Cl^- ions can be accommodated into the structure. For $x = 1$, as previously observed, reaction for one hour formed a rhombohedral phase. Decreasing the chloride content caused peak splitting in the X-ray diffraction pattern, which could be refined as a mixture of two rhombohedral phases. The presence of two phases in the product prevents accurate determination of the stoichiometry using the reactant ratios. The unit cell volumes of these two phases are shown in Figure 3 and show that the two rhombohedral phases have different cell volumes, with the larger likely to be chloride-rich and the smaller chloride-deficient. Decreasing x below 0.7 caused excess LiNH_2 to be observed alongside the rhombohedral phases in the diffraction pattern of the product, suggesting that no further decrease in chloride content can be accommodated.

After reaction for 12 hours, as described previously [5], a cubic $I2_13$ phase was observed at $x = 1$. As the chloride content was reduced, the unit cell volume of this cubic phase decreased (Figure 4). Decreasing x below 0.75 caused a rhombohedral phase also to be observed in the X-ray diffraction pattern of the product. This new phase was observed alone at $x = 0.57$, and has been characterized, through Rietveld refinement, as $\text{Li}_7(\text{NH}_2)_6\text{Cl}$ [12]. The unit cell volume of $\text{Li}_7(\text{NH}_2)_6\text{Cl}$ varied slightly in the range $x = 0.5\text{--}0.7$ suggesting that some deviation from the ideal stoichiometry may be possible, but much of the chloride excess was

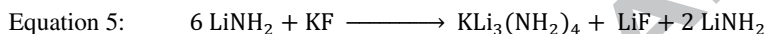
accommodated in the cubic phase for the $x = 0.7$ sample, and the chloride deficiency in an additional rhombohedral phase with a smaller unit cell for the $x = 0.5$ sample.

Lithium amide, $\text{Li}_4(\text{NH}_2)_3\text{Cl}$ and $\text{Li}_7(\text{NH}_2)_6\text{Cl}$ were each heated with LiH at 2°C min^{-1} to 400°C and the gases given off were monitored through mass spectrometry. Figure 5 shows that both chloride-containing samples released hydrogen at a lower temperature than LiNH_2 , with no deterioration of the properties seen on reduction of the chloride level. This reduction in chloride content increases the theoretical weight percent stored reversibly in the system (through reaction to the corresponding imide chlorides) from 4.4 to 5.4%.

3.4 Fluoride doping

With fluorine being the lightest of the halides, attempts were made to dope LiNH_2 with F^- . Reactions between LiNH_2 and LiF were carried out over a range of $\text{NH}_2^- : \text{F}^-$ ratios from 4:1 to 2:1, at temperatures up to 500°C , for reaction times of up to 3 days. Under these conditions, no change was observed in the diffraction patterns of the products when compared to those of the starting materials. It is thought that this was due to the high stability of LiF , making reaction with LiNH_2 thermodynamically disfavoured.

Potassium fluoride has a lower heat of formation than lithium fluoride, and so reactions between lithium amide and potassium fluoride were carried out for 12 hours at 400°C . The diffraction pattern of the products showed that a metathesis reaction had occurred, as described by equation 5 below.



Again, the stability of LiF appears to dictate the result of the reaction, preventing uptake of fluoride ions into the lithium amide structure.

4. Conclusion

The lower halide doping limits of lithium amide were investigated for the series of amide halides. It was found that no stoichiometry other than $\text{Li}_3(\text{NH}_2)_2\text{I}$ was observed in the iodide system and that an amide fluoride system was not obtained on reaction of LiNH_2 with LiF or KF . Lowering the bromide content in $\text{Li}_7(\text{NH}_2)_6\text{Br}$ led to a reduction in the unit cell volume, suggesting the accommodation of amide ions on some bromide sites in the structure. For the amide chloride system, $\text{Li}_4(\text{NH}_2)_3\text{Cl}$, a mixture of rhombohedral and cubic phases was observed except at the stoichiometry $\text{Li}_7(\text{NH}_2)_6\text{Cl}$, where a new phase was observed. This new low-chloride phase exhibited similar improved hydrogen desorption properties when compared to lithium amide as $\text{Li}_4(\text{NH}_2)_3\text{Cl}$, but with a much reduced weight penalty through addition of chloride.

5. Acknowledgments

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Figure Captions

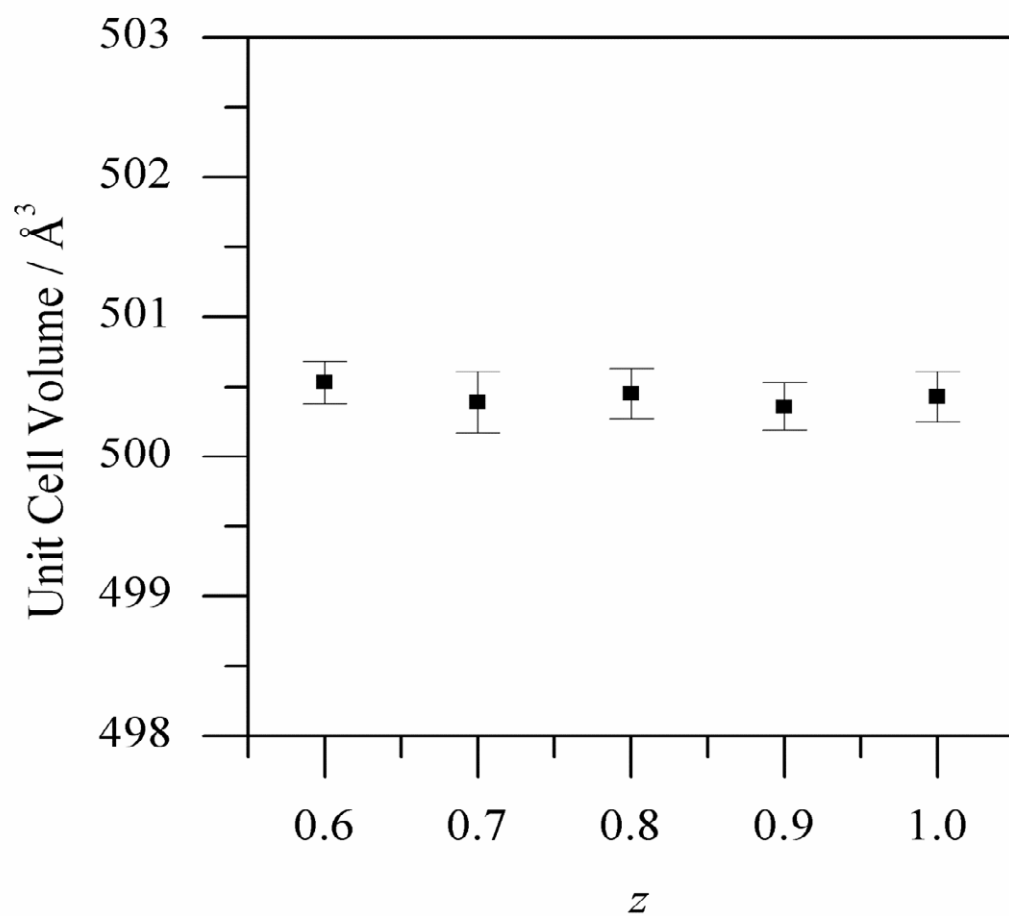
FIG1: Unit cell volumes and errors (3σ) for $\text{Li}_3(\text{NH}_2)_{(3-z)}\text{I}_z$

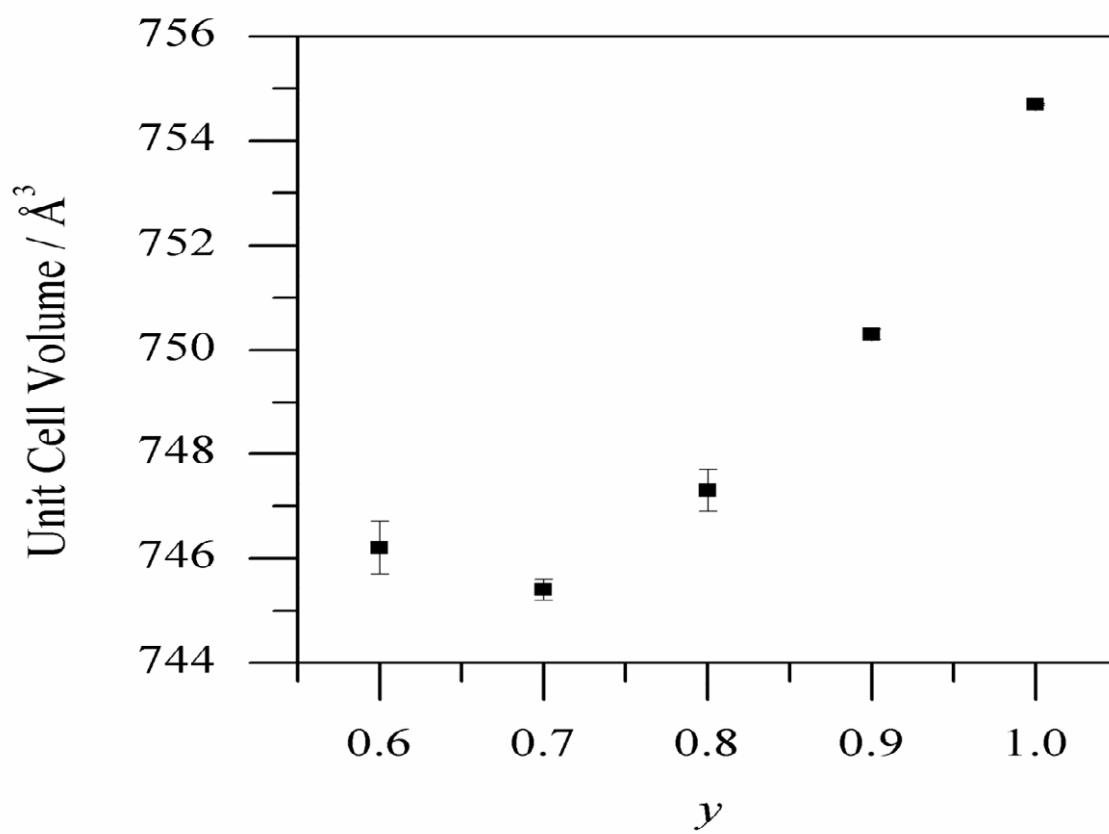
FIG2: Unit cell volumes and errors (3σ) for $\text{Li}_7(\text{NH}_2)_{(7-y)}\text{Br}_y$

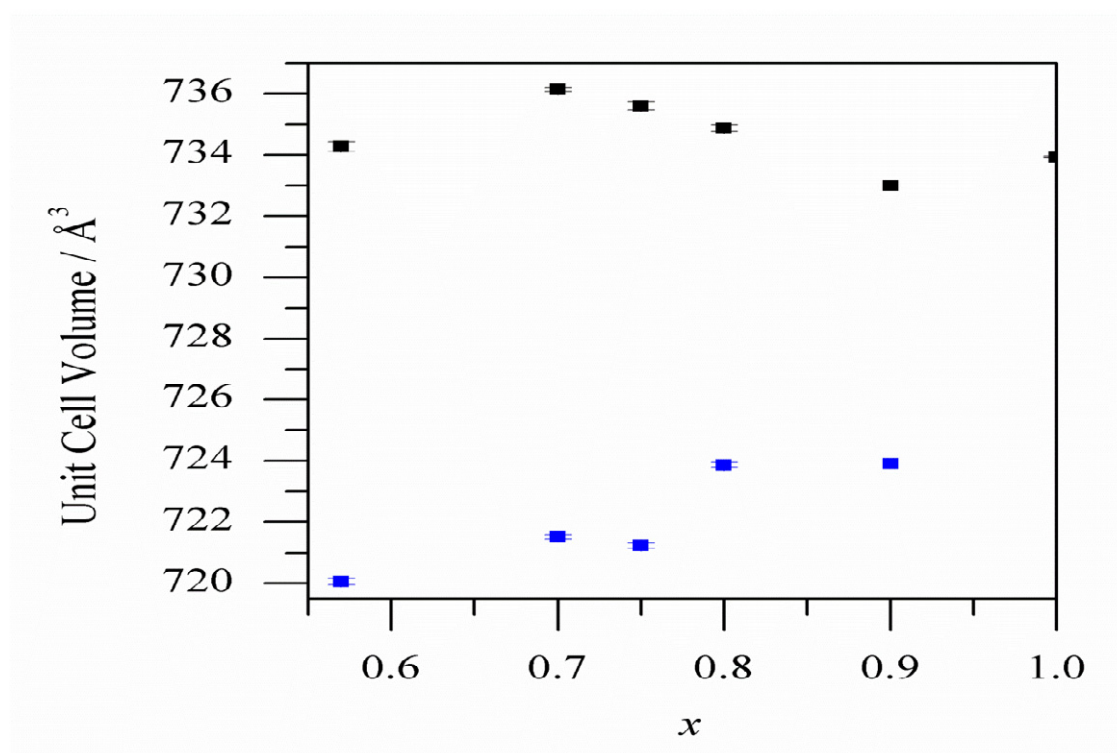
FIG3: Unit cell volumes and errors (3σ) for the two rhombohedral $\text{Li}_4(\text{NH}_2)_{(4-x)}\text{Cl}_x$ phases observed after a one hour reaction time.

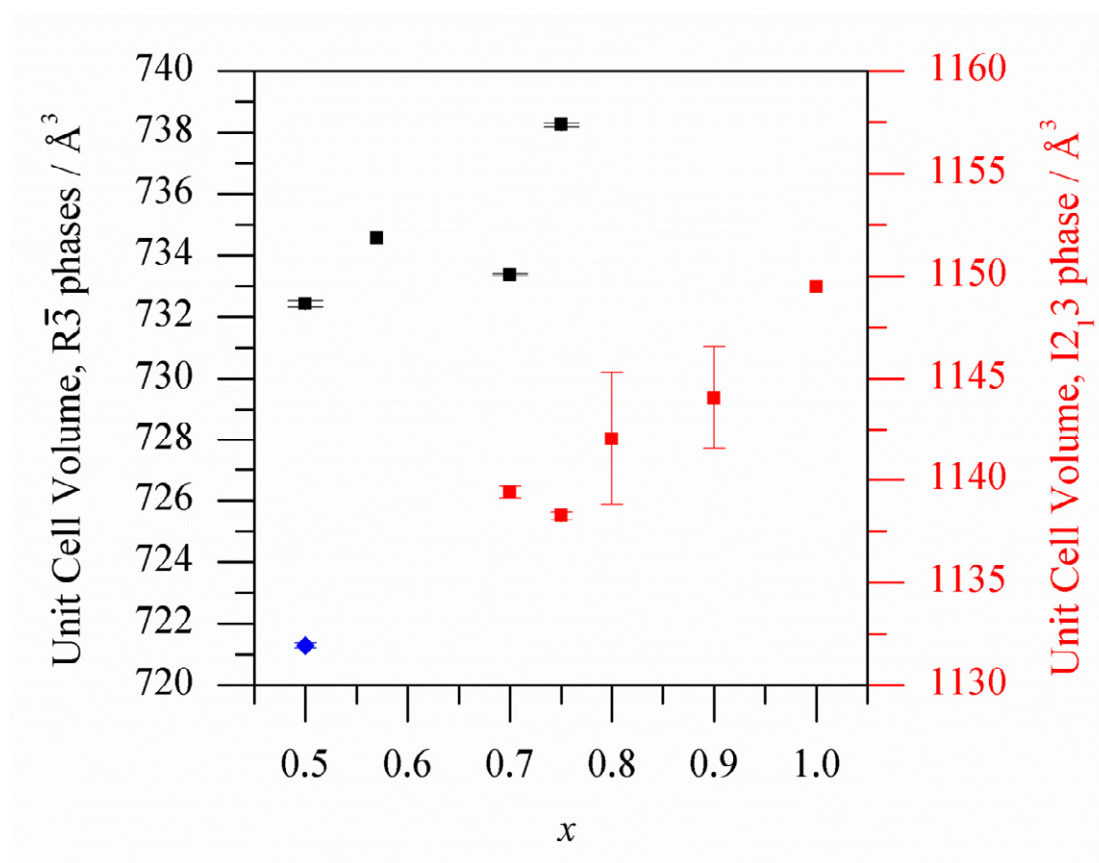
FIG4: Unit cell volumes and errors (3σ) for the different phases of $\text{Li}_4(\text{NH}_2)_{(4-x)}\text{Cl}_x$ after a twelve hour reaction time; the red points and axis correspond to the cubic phase that is formed, with the black and blue points and the black axis representing the two rhombohedral phases.

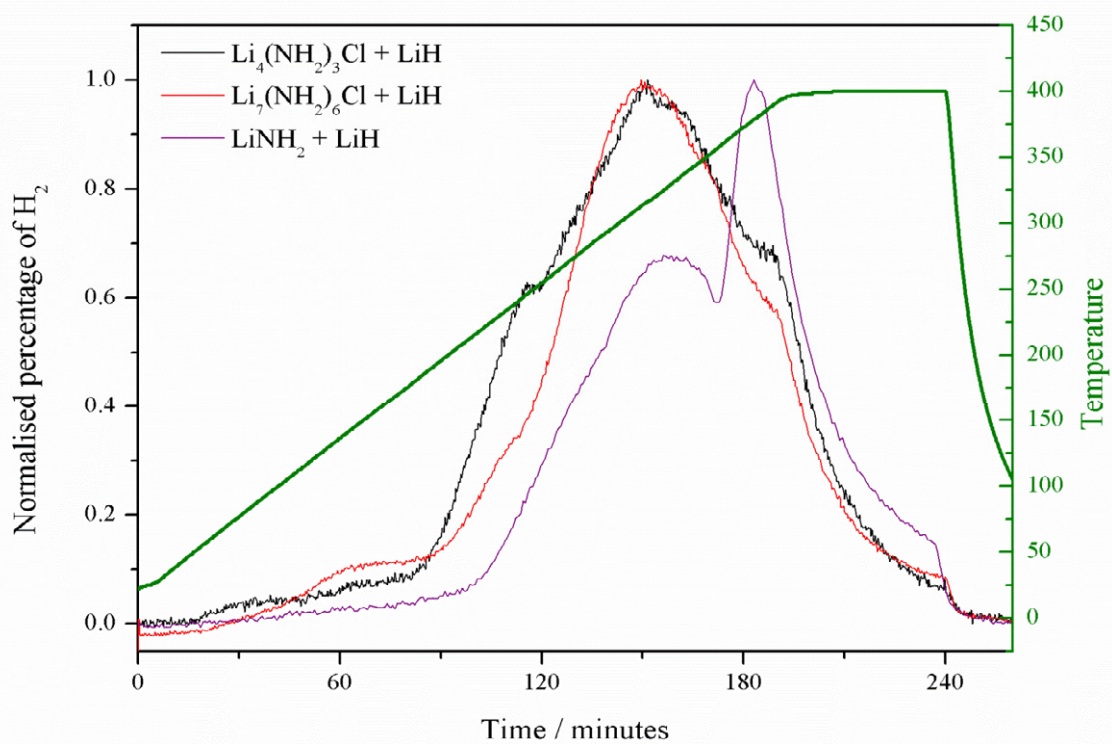
FIG5: TPD–MS traces for the lithium amide chlorides and lithium amide on reaction with lithium hydride.











Highlights

- The lower limits of halide incorporation in lithium amide have been investigated.
- The only amide iodide stoichiometry observed was $\text{Li}_3(\text{NH}_2)_2\text{I}$.
- Solid solutions were observed in both the amide chloride and amide bromide systems.
- A 46% reduction in chloride content resulted in a new phase: $\text{Li}_7(\text{NH}_2)_6\text{Cl}$.
- New low-chloride phase maintained improved H_2 desorption properties of $\text{Li}_4(\text{NH}_2)_3\text{Cl}$.